



1 **Importance of Biogenic Volatile Organic Compounds to Peroxyacyl** 2 **Nitrates (PANs) Production in the Southeastern U.S. during SOAS 2013**

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23

24 **Abstract**

25 Gas-phase atmospheric concentrations of PAN, PPN, and MPAN were measured at the ground using GC-
26 ECD during the SOAS 2013 campaign (1 June to 15 July 2013) in Centerville, Alabama in order to study
27 biosphere-atmosphere interactions. Average levels of PAN, PPN and MPAN were 169, 5, and 9 pptv
28 respectively, and the sum accounts for an average of 15% of NO_y during the daytime (10 am to 4 pm local
29 time). Higher concentrations were seen on average in air that came to the site from the urban NO_x sources
30 to the north. PAN levels were the lowest observed in ground measurements over the past two decades in
31 the Southeastern U.S. Analysis of PAN/NO_x indicates PAN production in this region was sensitive to NO_x.
32 A multiple regression analysis indicates that biogenic VOCs account for 66% of PAN formation in this
33 region of the Southeastern U.S. Comparison of this value with a 0-D model simulation of peroxyacetyl
34 radical production indicates that at least 50% of PAN formation is due to isoprene oxidation. MPAN has a
35 statistical correlation with isoprene hydroxynitrates (IN) with an average MPAN_{ppb}/IN_{ppb} ratio of 0.3.
36 Organic aerosol mass increases with gas-phase MPAN and IN concentrations, but the mass of organic



1 nitrates in particles is largely insensitive to MPAN. Isoprene and PAN play a significant role in the
2 atmospheric chemistry in the Southeastern United States.

3 **1. Introduction**

4 The Southern Oxidant and Aerosol Study (SOAS), part of the Southeast Atmosphere Study (SAS) in 2013,
5 focused on biosphere-atmosphere interactions and the subsequent influences of biogenic volatile organic
6 compounds (BVOCs) on atmospheric oxidant chemistry and aerosol formation. Since natural emissions of
7 organic compounds in the Southeast are high and there are a variety of anthropogenic pollution sources, the
8 location is ideal to study biogenic-anthropogenic interactions (Carlton et al., 2018).

9 Peroxyacyl nitrates (PANs, RC(O)OONO_2), products of the photooxidation of VOCs in the presence of
10 nitrogen oxides (NO_x), play an important role in gas and particle tropospheric chemistry. PANs account for
11 a significant amount of NO_y in rural and forested areas in the Eastern United States (Trainer et al., 1993),
12 affect the lifetime of NO_x , enhance O_3 formation (Carter et al., 1981), contribute to human health issues,
13 and are known to be phytotoxic (Finlayson-Pitts and Pitts, 2000; Kleindienst et al., 1990).

14 Peroxyacetyl nitrate (PAN) is the simplest and most abundant of the PANs and peroxypropionyl nitrate
15 (PPN) and peroxymethacryloyl nitrate (MPAN) also are observed in the field (e.g. Nouaime et al., 1998;
16 Pippin et al., 2001; Roberts, 2002). PAN is formed from both anthropogenic and biogenic hydrocarbon
17 precursors. PPN, on the other hand, is formed primarily from anthropogenic hydrocarbons (AHCs) (e.g.
18 propanal, propane, 1-butene) while MPAN is derived from methacrolein (MACR), an oxidation product of
19 the mostly biogenic hydrocarbon (BHC), isoprene (Biesenthal and Shepson, 1997; Carter and Atkinson,
20 1996).

21 Recent laboratory experiments have suggested that OH reaction with the double bond of MPAN could be
22 involved in the formation of secondary organic aerosol (SOA) (Chan et al., 2010; Kjaergaard et al., 2012;
23 Lin et al., 2013; Nguyen et al., 2015; Surratt et al., 2010; Worton et al., 2013). This pathway is currently
24 treated in a few models that include isoprene (e.g. Pye et al., 2013; Pye et al., 2015; Jenkin et al., 2015;
25 Wennberg et al., 2018), although because isoprene is the biogenic non-methane hydrocarbon with the
26 greatest global emission rate (Guenther et al., 1995), the contribution of isoprene photooxidation to aerosol
27 radiative forcing may be underestimated. We currently do not know the partition coefficient of MPAN with
28 the particle phase, and little about condensed phase chemistry of MPAN.

29 We measured PANs concentration during the SOAS 2013 campaign to characterize the systematic
30 behavior and levels of individual PAN species at an urban-impacted forest and to assess the current state of
31 the attribution of PANs formation to biogenic and anthropogenic precursors quantitatively using several



1 statistical methods. Finally, we compared MPAN with another nitrogen compounds in the gas phase, total
2 isoprene hydroxynitrates (IN) and with organic nitrates or total organic aerosol (OA) in the particle phase
3 to investigate relationships that might explain their influence on SOA formation.

4 2. Experimental

5 Ground-based measurements were conducted from 1 June to 15 July 2013 at the Southeastern Aerosol
6 Research and Characterization (SEARCH) Centreville (CTR) site, which was located in a forested area in
7 the Talladega National Forest near Brent, Alabama, (lat: +32°54'11.81", long: -87°14'59.79). The major
8 anthropogenic influence at this site comes from the cities of Tuscaloosa and Birmingham, which are located
9 50 km northwest and 80 km northeast respectively.

10 Measurements of PANs using similar methods to those described below were made in Dickson, TN from
11 15 June to 14 July, 1999 as part of the Southern Oxidants Study (SOS) (Cowling et al., 1998) and are
12 referred to in the text. The site is located near Montgomery Bell State Park about 60 km west-southwest
13 (upwind) of downtown Nashville (Chen, 2001). While in a different part of the southeast, we believe that
14 the distance from major urban areas makes this site a good comparison.

15 PANs were quantified using a custom gas chromatograph (GC) equipped with a Shimadzu GC-Mini-2
16 ⁶³Ni electron capture detector (ECD) maintained at 55 °C (described by (Nouaime et al., 1998)). A polar
17 column (RESTEK, Rtx-200, 15 m x 0.53 mm ID x 1 μm) was kept at 15 C° to minimize thermal
18 decomposition of PAN compounds. Helium was used as carrier (8 cm³ min⁻¹) with N₂ make-up gas (3 cm³
19 min⁻¹). Ambient air was drawn through a ¼" OD PFA Teflon tube from 8.2 m height above the ground at 1
20 SLPM and a sub-sample of this air was drawn through a 1 cm³ sample loop at 50 sccm. The residence time
21 was approximately 9 sec. The sample loop contents were injected into the column at 20 min intervals via a
22 6-port Teflon valve (Hamilton). The baseline and sensitivity of the GC-ECD were checked every day during
23 the campaign using standard addition of gas streams from liquid standards added to ambient air scrubbed
24 through a charcoal trap at the beginning of the sampling line. In this way, the impact of the inlet line was
25 accounted for in the calibration. Separate calibrations were performed with synthetic PAN, PPN, and
26 MPAN samples in dodecane or tridecane maintained at ice water temperature in diffusion cells. The level
27 of PAN in each synthetic compound was determined with a chemiluminescence NO_x analyzer (Themo
28 Environmental Instruments, Inc., Model 42S) equipped with a Mo converter held at 325°C. The converter
29 efficiency was tested by O₃ titration of NO to NO₂. Calibration of the NO_x analyzer was done against a
30 NIST-traceable cylinder of 2ppmv NO in N₂ (SCOTT-MARRIN, INC). Based on sensitivity and
31 background measurements, the detection limits (S/N=2) for PAN, PPN and MPAN were estimated as 2.5



1 pptv, 3.6 pptv and 3.9 pptv, respectively. Uncertainty determined by error propagation, most of which came
2 from the chemiluminescence NO_x analyzer, was estimated to be 20% RSD.

3 Measurements of other trace gases, such as NO_y, NO_x, and O₃, wind direction, temperature, and boundary
4 layer height were made by Atmospheric Research & Analysis, Inc. (ARA) as described by Hidy et al. (2014).
5 Total isoprene hydroxynitrate (IN) concentrations were determined by Purdue University using a chemical
6 ionization mass spectrometer (CIMS) with operating conditions described by Xiong et al. (2015). MACR
7 was measured by NOAA ESRL Chemical Sciences Division and University of California, Berkeley
8 (Goldstein group) using a GC-MS. Particle-phase organic nitrates (pONs) were measured by University of
9 California, Berkeley (Cohen group) using thermal dissociation laser-induced fluorescence (TD-LIF),
10 described by Rollins et al. (2010), and by University of Colorado with a high resolution time of flight
11 aerosol mass spectrometer (HR-ToF-AMS) described by DeCarlo et al. (2006) and Hu et al. (2015). A
12 comparison in Lee et al. (2016) found that the pONs-TD-LIF was generally higher by factor ~5 than pONs-
13 HR-ToF-AMS. Both sets of data provide a reasonable range of pONs concentration. Total OA mass was
14 measured using HR-ToF-AMS. Data below detection limit were excluded from statistical analysis.

15 Comparison of PANs measurements among WMU, ARA, and UC Berkeley

16 During the SOAS 2013 campaign, two other research groups measured the sum of total PANs without
17 identification of each species. ARA measured total PANs using thermal dissociation into NO₂ at 160 °C on
18 top of ambient NO₂ located within 30 m of the WMU instrument and at the same height. The Berkeley
19 group measured total PANs using thermal dissociation from the tower approximately 100 m north of the
20 WMU instrument and approximately 25 m above the ground. Total PANs from all three groups showed
21 statistically significant ($p < 0.01$) positive linear correlations with each other based on results from
22 Spearman's rank correlation test (a nonparametric test was used due to non-normal distributions). The
23 correlation coefficient, r_s of each pair (PAN_{SWMU} vs. PAN_{SARA}, PAN_{SWMU} vs. PAN_{SUC}, and PAN_{SARA} vs.
24 PAN_{SUC}) was 0.754, 0.926, and 0.714 respectively. However, a Friedman test resulted in statistically
25 different medians of PANs from three groups. The relationships with PAN_{SWMU} are plotted in Figure S1.
26 Overall, the measurement of PAN_{SUC} was 50% greater than PAN_{SWMU}, while the measurement of PAN_{SARA}
27 was 30% less than PAN_{SWMU}. The strong statistical correlation of all datasets allows the investigation of
28 PANs behavior despite the systematic differences.

29 3. Results

30 3.1 General behavior of PANs in 2013



1 Figure 1 shows a time series of PAN, PPN, and MPAN throughout the campaign. Data that were below
2 detection limit (BDL) are plotted at half of the reported detection limit for that compound. This was done
3 to distinguish the BDL points from missing data due to tests, calibrations, and the periodic existence of a
4 noise interference that often appeared during this campaign and could not be eliminated, and to not lose the
5 low concentration information content. Relatively high levels of PAN were observed as periodic spikes
6 during the campaign, but overall PAN levels were lower than most other measurements in the southeast
7 made over the last 20 years. A local biomass burning event was observed on June 4th (Washenfelder et al.,
8 2015), which resulted in an unusually high level of PAN of around 1600 pptv and an extreme deviation
9 from the median. Hence, the data on June 4th was removed from statistical analyses.

10 General descriptive statistics for all daytime data are summarized in Table 1. Daytime was defined as 10
11 am to 4 pm local time (CDT). PAN was consistently the most abundant peroxyacyl nitrate compound and
12 the mean concentration during daytime was 34 and 19 times larger than that for PPN and MPAN,
13 respectively. In Table 1, “PANs” describes the sum of individual PAN, PPN, and MPAN values. The
14 average of the ratio of PANs/NO_y during daytime was 0.15. Peroxyacryloyl nitrate (APAN) was also
15 observed occasionally during the campaign. APAN has been proposed to arise from 1,3-butadiene, either
16 from anthropogenic sources or biomass burning, and from direct emission of acrolein (Roberts et al., 2001;
17 Tanimoto and Akimoto, 2001). Our data did not show a strong relationship to biomass burning events, as
18 identified by Washenfelder et al. (2015), although an instrument interference problem limited the amount
19 of reportable APAN data, so no clear conclusion can be drawn.

20 Although surface air most frequently came from the south during the SOAS 2013 campaign, air from the
21 north contained levels of PANs that were twice as large as from south. The averages of PAN, PPN, and
22 MPAN with air from the north were 182, 5.3, and 8.4 pptv respectively, while averages of air from south
23 showed 94.6, 2.8, and 3.6 pptv. Polar plots of PAN, PPN and MPAN as a function of surface wind direction
24 are shown in Figure S3 with wind frequency. This elevated northern distribution is also seen with NO_x and
25 O₃ reflecting the influence of anthropogenic pollution sources from Tuscaloosa, Birmingham, and Atlanta.

26 Plots of diurnal mean and median values separated by surface wind direction (Figure 2) indicate a
27 noticeable pattern in PAN, PPN, and MPAN from the north and a much weaker pattern in southerly air.
28 Levels of all three PANs were highest (also with greatest variance) during the daytime on average. It was
29 difficult to see the mean and median diurnal cycle for PPN because of very low concentrations observed
30 over the campaign. The PAN diurnal pattern was generally similar to those reported for Nashville in 1995
31 and 1999 (Nouaime et al., 1998; Roberts, 2002). A calculation using ambient temperature and [NO]/[NO₂]
32 shows that the effective PAN thermal decomposition lifetime changes little over the course of the afternoon,



1 which suggests that PAN levels fluctuate during early afternoon mostly due to dilution by boundary layer
2 growth (boundary layer height increased by a factor of 2-3 from 9am to noon-3pm on average based on a
3 LIDAR measurements).

4 **3.2 Historical PANs measurements in the Southeastern US over last 23 years**

5 PAN compounds have been measured at various rural and urban locations within the Southeastern U.S.
6 over the last 23 years. Observations from six sites, Elberton (GA) 1990; ROSE (AL) 1990 and 1992; New
7 Hendersonville (TN) 1994; Youth Inc. (TN) 1995; Dickson (TN) 1999; Cornelia Fort Airpark (TN) 1999
8 (Nouaime et al., 1998; Roberts, 2002; Roberts et al., 1998) are compared here with SOAS 2013 data (a map
9 of the locations is shown in Figure S2).

10 Binned PAN concentrations during the daytime (10 am – 4 pm) are plotted as a function of the concentration
11 of NO_x (grouped into deciles) in Figure 3a. Urban areas have higher PAN concentration with higher NO_x
12 than rural areas. The only site specially revisited was ROSE, where PAN levels in 1990 were more than
13 twice as high as in 1992. Hence, the PAN concentrations can vary depending on place and year. A curve fit
14 to the data in Figure 3a shows an asymmetric peak in the concentration that appears to peak at around 3.5
15 ppb NO_x . PAN concentration increases approximately linearly with NO_x up to 2 ppb and beyond the peak
16 it decreases slowly with further increases in NO_x . Similar behavior was observed in the relationship between
17 O_3 and NO_x concentration in Figure 3b and the peak was at around 1.5 ppb NO_x .

18 The relationship of O_3 production with NO_x and VOC concentrations is typically discussed in terms of
19 “ NO_x -limited” and “VOC-limited” regimes, (Finlayson-Pitts and Pitts, 2000; Milford et al., 1994;
20 Chemeides et al., 1992), although there has been less discussion of the sensitivity of PAN production to
21 these reactants. This curve is reminiscent of the modeled O_3 production rate as a function of NO_x and HO_x
22 in Thornton et al. (2002) from OH oxidation of VOC based on measurements from Cornelia Fort Airpark
23 in 1999. At low NO concentration, an increase of O_3 production rate with NO occurred, since OH is
24 generated via $\text{HO}_2 + \text{NO}$ and the primary chain termination are $\text{HO}_x + \text{HO}_x$ reactions. On the other hand, O_3
25 production rate slows at high NO concentrations. In this NO_x -saturated (VOC-limited) regime, OH is
26 consumed, because $\text{HO}_x + \text{NO}_x$ reactions and $\text{RO}_2 + \text{NO} \rightarrow \text{RONO}_2$ (Romer et al., 2016) become faster than
27 $\text{HO}_x + \text{HO}_x$ reactions. The peak is related to the crossover point between NO_x -limited and NO_x -saturated. A
28 high HO_x production rate (radical-limited conditions) enhances the O_3 production rate with NO for low NO
29 and the crossover point shifts to higher NO.

30 As a significant covariance between PAN and O_3 has been reported (Bottenheim et al., 1994), the behavior
31 of the relationship of PAN vs. NO_x could result from similar sensitivity of PAN production as O_3 production.



1 A linear increase of PAN concentrations with NO_x at low NO_x in Figure 3a could result from the chemistry
2 in the NO_x-limited regime and most PAN concentrations at rural sites were dependent on NO_x
3 concentrations. The slow decrease of PAN concentration at higher NO_x levels such as those seen at more
4 urban sites results from faster radical termination rates, and thus VOC oxidation rates slow. This
5 empirically-derived distinction is likely related to differences in reaction rates with peroxy radicals that
6 could be investigated computationally. PAN, O₃ and NO_x levels in the Southeast were all lowest at SOAS
7 2013. As NO_x levels continue to decrease in the US with more stringent emission standards and conversion
8 to non-fossil energy sources, PAN production rate might become more widely sensitive to NO_x.

9 3.3 Anthropogenic vs Biogenic contribution to PAN production

10 3.3.1 Description of MLR and its Statistical Meaning

11 A multiple linear regression (MLR) has been used to quantify PAN sources (Roberts, 2002; Roberts et al.,
12 1998; Williams et al., 1997). Since the thermal decomposition rates of PANs are similar (Roberts and
13 Bertman, 1992), and MPAN and PPN are formed from BHC and AHC respectively and PAN is formed
14 from both, [PAN] can be approximately represented as a weighted linear combination of [MPAN] and
15 [PPN]. The combination of BHC and AHC chemistry is indicated by MPAN and PPN. The linear model is
16 applied as in equation 1.

$$17 [PAN] = A + B_1[MPAN] + B_2[PPN] \quad (1)$$

18 Here, A is the intercept and B_1 and B_2 are partial regression coefficients, estimated using a computer
19 software program based on field observations. The MLR statistical analysis includes estimation of A , B_1
20 and B_2 , overall F -test and a t -test, and diagnostic procedures (e.g. Mendenhall et al., 2008). The F -test is
21 used to investigate the statistical significance of the model in Equation (1) using an analysis of variance
22 (ANOVA) table. The strength of the model is evaluated using the coefficient of determination R^2 between
23 predicted and measured [PAN] (also provided through this statistical analysis). The individual t -test, which
24 is based on the Student's t statistic, is used to investigate the statistical significance of the individual B_1 and
25 B_2 . In a MLR statistical analysis, the magnitude of the standardized partial regression coefficients, β_i , which
26 is calculated as a product of partial regression coefficient and the ratio between the standard deviation of
27 the respective independent variable (MPAN or PPN) and the standard deviation of the dependent variable
28 (PAN), is frequently used to compare the relative contribution of independent variables. The results of MLR
29 statistical analysis are summarized in Tables S1 and S2.

30 Tatsuoka (1971) showed that R^2 from the MLR is equal to the sum of the product of the β_i and the zero-
31 order (simple bivariate) correlation, r_i , which are obtained as results of MLR (see Table S2). That is, $R^2 =$



1 $\sum \beta_i r_i$. Therefore, we used the fraction of R^2 based on the strength of relationship in each [MPAN] and
2 [PPN] to [PAN] to describe the relative importance of BHC and AHC. Each partial R^2 is obtained as shown
3 in equations 2 and 3.

$$4 \quad R^2_{BHC} = \beta_1 r_{MPAN vs. PAN} \quad (2)$$

$$5 \quad R^2_{AHC} = \beta_2 r_{PPN vs. PAN} \quad (3)$$

6 This approach allows us to directly treat the R^2 in the MLR to assess the relative importance of BHC and
7 AHC, including the strength of correlation with PAN.

8 Results from SOAS were compared with similar PAN data collected from Dickson, TN in 1999, another
9 rural southeastern site, which show that the MLR model and regression coefficients for both MPAN and
10 PPN at both sites were statistically significant (see Tables S1 and S2). During SOAS 2013, 60% of the
11 variance in the measurements was explained by the MLR model. At the Dickson site in 1999, 77% of the
12 variance was explained by the MLR model. The R^2 of MLR in the SOAS 2013 data was lower than that in
13 Dickson 1999, which might result from the lower absolute PANs levels during SOAS 2013. In particular,
14 SOAS MPAN and PPN data included a large number of below detection limit measurements, while Dickson
15 1999 data did not. The medians of PAN, MPAN, and PPN in Dickson 1999 (483.5, 25.4, and 24.7 pptv
16 respectively) were three times higher than the medians for SOAS 2013. Also, in Dickson 1999, NO_x levels
17 were seven times higher. In Figure 4, the relative importance of BHC and AHC was standardized to compare
18 SOAS 2013 and Dickson 1999. Standardized relative percentiles were calculated as $R^2_{BHC}/R^2 \times 100$ for BHC
19 and $R^2_{AHC}/R^2 \times 100$ for AHC. Biogenic influence accounted for 66% of PAN during SOAS 2013 and was
20 two times larger than the anthropogenic influence. This is the opposite of results from Dickson where the
21 biogenic influence accounted for only 25% of PAN. Although both sampling locations were located in rural
22 areas in similar environments, the results using MLR indicate that the HC precursors were different.

23 3.3.2 Comparison of contribution of isoprene oxidation with computational modeling

24 We used two computational approaches to assess the contribution of isoprene oxidation to PAN formation
25 by 1) orthogonal distance regression (ODR) between field measurements of MPAN and PAN and 2)
26 simulation of the production of peroxyacetyl (PA) radicals, precursors of PAN, using an ambient 0-D
27 photochemical model.

28 In ODR, the fraction of PAN production from isoprene oxidation can be expressed as
29 $(d[\text{PAN}]_{\text{isoprene}}/dt)/(d[\text{PAN}]_{\text{all}}/dt)$. Assuming that MPAN is solely derived from isoprene oxidation, the
30 relative yield of $(d[\text{MPAN}]/dt)/(d[\text{PAN}]_{\text{isoprene}}/dt)$ was obtained from an isoprene oxidation chamber



1 experiment as 0.15 ± 0.03 RSD. The reaction was initiated with 1.37 ppm isoprene, 268 ppb NO, and 206
2 ppb NO₂ under 5% RH in a 5.5 m³ Teflon cylindrical bag. The OH radical was produced by photolysis of
3 HONO. The fraction of PAN production from isoprene oxidation to total PAN formation in the field was
4 rearranged as the following equation.

$$5 \quad \frac{d[\text{PAN}]_{\text{isoprene}}/dt}{d[\text{PAN}]_{\text{all}}/dt} = 6.7 \times \frac{d[\text{MPAN}]/dt}{d[\text{PAN}]_{\text{all}}/dt} \quad (4)$$

6 The $(d[\text{MPAN}]/dt)/(d[\text{PAN}]_{\text{all}}/dt)$ was obtained from measurements in SOAS 2013 as the slope of the linear
7 regression line of [PAN] to [MPAN].

8 In the 0-D photochemical model simulation, the relative contribution to peroxyacetyl (PA) radicals from
9 VOCs present at the field site is based on the Master Chemical Mechanism (MCM) v3.3. The ambient
10 model included not only isoprene and its oxidation products (including CH₃C(O)CHO) but also acetone,
11 acetaldehyde, and some mono-terpenes as precursors. The detail of the parameters for MCM set are
12 described in Groff (2015).

13 These two methods were compared with the relative importance of BHC, $\beta_{1r_{\text{MPANvs.PAN}}}$, from the MLR
14 model in this work. Four days (Jun 3rd 12:30 – 18:00, Jun 14th 11:30 – 18:00, Jun 26th 11:00 – 18:00, and
15 Jul 12th 13:00 – 18:00) of data from SOAS 2013 were selected to run the 0-D model because the production
16 ratio using ODR can only be used when PAN, MPAN and NO_x concentrations were appropriately high.
17 The time ranges were chosen so that the boundary layer height would be stable and any dilution effect
18 would be minimal. Results of the comparison are plotted in Figure 5. Although the relative importance of
19 BHC in the MLR model was less than 40% on June 3rd, it was statistically dominant on the other three days
20 accounting for more than 68%. (Note: PPN on June 3rd did not have a significant level to predict PAN in
21 MLR analysis, $p=0.600$.) By comparison, the estimated contribution of isoprene oxidation using ODR on
22 June 3rd had the steepest slope, however, the range of the 95% confidence interval (C.I.) on this day was
23 large. On the other three days, the relative contributions of isoprene oxidation using ODR were estimated
24 at 23 – 49%, lower than the results derived from the other two methods. This might be due to the differences
25 between the chamber experiment and ambient conditions. Specifically, the ratio of secondary to primary
26 oxidation products varies between chamber and ambient conditions, with likely relatively greater primary
27 products under chamber conditions. Since PAN is formed via the oxidation of secondary products of
28 isoprene, the $[\text{MPAN}]/[\text{PAN}]_{\text{isoprene}}$ ratio would be higher in the chamber experiment than in ambient
29 environment. This ratio is expected to derive results that are biased low, when used to estimate the ambient
30 isoprene-derived PAN concentration. In addition, photolysis rates also are significantly different between
31 the chamber and the field conditions. The results of the 0-D model suggest that isoprene oxidation
32 significantly contributed to PAN formation with a mean range of 55–73% over all selected days. The



1 relative contribution of isoprene oxidation determined by PA radicals was typically 7–25% lower than by
2 MLR model analysis on three days, except June 3rd. Hence, both methods, the MLR and the 0-D model,
3 indicate that isoprene oxidation was the main source when high levels of PAN were observed during SOAS
4 2013.

5 **4. Discussion**

6 **4.1 Comparison among MACR, IN, and MPAN**

7 MACR is a first generation product of isoprene photooxidation mechanisms, and MPAN is derived from
8 MACR oxidation (Bertman and Roberts, 1991; Kjaergaard et al., 2012). With enough NO_x, the OH adduct
9 of isoprene that is the precursor to MACR in these mechanisms is also a precursor of gas-phase isomers of
10 isoprene hydroxynitrates (IN) (Shepson, 2007; Grossenbacher et al., 2001, 2004; Barker et al., 2003; Paulot
11 et al., 2009; Lockwood et al., 2010). Xiong et al. (2015) reported IN at SOAS, which affords the opportunity
12 to study this aspect of NO_x sensitivity of isoprene oxidation. In this work, the daytime (10 am – 4 pm)
13 relationships among MPAN, MACR and IN at SOAS was investigated using the Pearson's correlation
14 statistical test. Missing data was treated as pairwise deletion (not listwise deletion). The correlation
15 coefficient between the first generation products of isoprene, MACR and IN was 0.528 ($p < 0.001$) and
16 indicated a statistically significant positive correlation. According to the known chemical pathways, a strong
17 relationship is expected between MACR and MPAN, while a weak relationship is expected between IN and
18 MPAN given that IN is a primary product, while MPAN is secondary. The results show, however, that
19 daytime data over the whole campaign did not show significant correlation between MACR and MPAN (r
20 $= 0.148$, $p = 0.104$). In contrast, IN has a statistically significant positive correlation with MPAN ($r = 0.499$,
21 $p < 0.001$). The average ratio of MPAN_{ppb}/IN_{ppb} was 0.3 (± 0.04), based on the slope of [MPAN_{ppb}] vs.
22 [IN_{ppb}] ($p < 0.001$, with a slope significantly different from 0). Likely this relationship is a result of the NO_x
23 dependence of both organic nitrate products. Because MACR can be produced in the absence of NO_x,
24 MPAN is more dependent on NO_x than on MACR at this site, and isoprene nitrates constitute a larger
25 fraction of gas-phase organic nitrates from BVOC than MPAN does. This is consistent with the Romer et
26 al. (2016) work showing that IN production is the dominant sink for both radicals and NO_x in the daytime
27 at this site.

28

29 **4.2 Gas-phase MPAN vs. organic aerosol mass – is there evidence that MPAN leads to more**
30 **organic mass and does the nitrogen from MPAN stay in particle?**



1 During SOAS 2013, Lee et al. (2016) estimated that the particle-phase organic nitrates (pONs) accounted
2 for 3% of total organic aerosol (OA) mass, on average, during the day (12 pm – 4pm) and BVOC precursors
3 strongly impacted the diel trends of pONs. Laboratory experiments suggest that MPAN can play a key role
4 in SOA formation under high NO_x conditions. C4-hydroxynitrate-PAN or hydroxymethyl-methyl- α -
5 lactone (HMML) (Kjaergaard et al., 2012; Nguyen et al., 2015; Wennberg et al., 2018) have been proposed
6 as key precursors for uptake into the particle-phase from MPAN oxidation. Nguyen and co-workers (2015)
7 estimated the SOA yield as approximately ~60 % by mole from MPAN + OH reaction in the absence of
8 NO_x . IN is also expected to contribute to SOA formation (Jacobs et al., 2014). If organic nitrates are
9 involved in SOA formation, gas-phase MPAN and IN should be related to particle mass, although the
10 nitrogen could be unretained in the particle. Figure 6 shows the relationship of gas-phase MPAN and IN
11 with daytime particle measurements to investigate if nitrogen from these organic nitrates was retained in
12 particles and if they are correlated with total OA without organic nitrates.

13 As MPAN and IN concentrations increase, Figure 6 shows that OA mass increases, while pONs mass
14 increases very little (measured by both HR-ToF-AMS and TD-LIF), although the slopes of MPAN and IN
15 vs. pONs are statistically different from zero. The relative magnitude of the response of OA and pONs to
16 increases in MPAN and IN suggests that they contribute to OA growth more strongly than to pONs growth.
17 Although this may suggest that if MPAN oxidation by OH is involved in particle growth, the nitrogen from
18 MPAN is not represented in aerosol organic nitrate. Oxidation of MPAN modeled from MACR + OH results
19 at FIXCIT (Nguyen et al., 2014) using measured total peroxy nitrates and kinetics of the isoprene mechanism
20 in MCM v3.3.1 (Jenkin et al., 2015) showed a positive relationship between MPAN oxidation and pONs
21 formation, although with a yield <3% (P. Romer, personal communication). Results of direct reaction of
22 MPAN + OH suggest that it is unlikely that pONs formation is mainly derived from MPAN+OH reaction,
23 even in the presence of NO_x (Nguyen and Wennberg, personal communication). This small contribution of
24 isoprene oxidation compounds to pONs formation is consistent with reported modelling of pONs formation
25 (Xu et al., 2015; Ayres et al., 2015; Pye et al., 2015). Ayres et al. suggest that pONs formation at SOAS
26 was dominated by nighttime reactions of NO_3 radicals with BVOCs rather than daytime reactions, and more
27 from monoterpene oxidation than isoprene oxidation.

28 Rather, MPAN is likely a precursor to low vapor pressure products that undergo aerosol uptake (perhaps as
29 a HMML precursor). The correlation between INs and MPAN with OA likely reflects that much of the OA
30 derives from BVOC oxidation, and the conditions that lead to large rates of BVOC emission and oxidation
31 (high T and radiation) simultaneously produce OA, along with INs and MPAN. That OA does not correlate
32 well with condensed phase organic nitrate reflects the fast hydrolysis of organic nitrates in the aerosol phase



1 at low aerosol pH (Rindelaub et al., 2016; Jacobs et al., 2014; Guo et al., 2015). While organic nitrates such
2 as the INs may partition to the aerosol phase, they are quickly converted to inorganic nitrate ion and other
3 products by hydrolysis.

4 **5. Conclusions**

5 The level of PAN compounds measured at the ground site during SOAS 2013, is lower than data measured
6 in the Southeastern U.S. over the past two decades. We show here that PAN concentrations are highly NO_x
7 sensitive. Russell et al. (2012) show that NO_x in the eastern US has been decreasing rapidly, due to effective
8 emission control, and thus this has effectively also decreased PAN production. As this process continues,
9 PAN may continue to be a smaller fraction of NO_y, as peroxy radicals such as CH₃C(O)OO react with HO₂
10 and RO₂ rather than with NO_x. PAN appears to be most sensitive up to [NO_x] approximately 3.5 ppb, above
11 which PAN concentrations switch to a NO_x-saturated (or VOC-limited) regime. So, PAN production during
12 SOAS was highly sensitive to NO_x concentration and this was particularly observed in the biogenically
13 derived MPAN formation. Overall, MPAN did not show a statistically significant correlation with MACR,
14 but did show a statistically positive correlation with IN. These results indicate that both organic nitrate
15 products were NO_x dependent (MPAN being more sensitive to NO_x than to MACR precursor) and IN
16 production might be the dominant sink for both radicals and NO_x in the daytime at this site.

17 We estimate that biogenic precursors, particularly isoprene, account for about 66% of PANs, twice as much
18 as anthropogenic influence during the overall campaign and that gas-phase MPAN shows significant
19 contribution to OA growth, but less contribution to pONs during the daytime. This may suggest that the
20 nitrogen of MPAN is removed during oxidation to other low vapor pressure products, consistent with the
21 HMML mechanism first suggested by Kjaergaard et al (2012).

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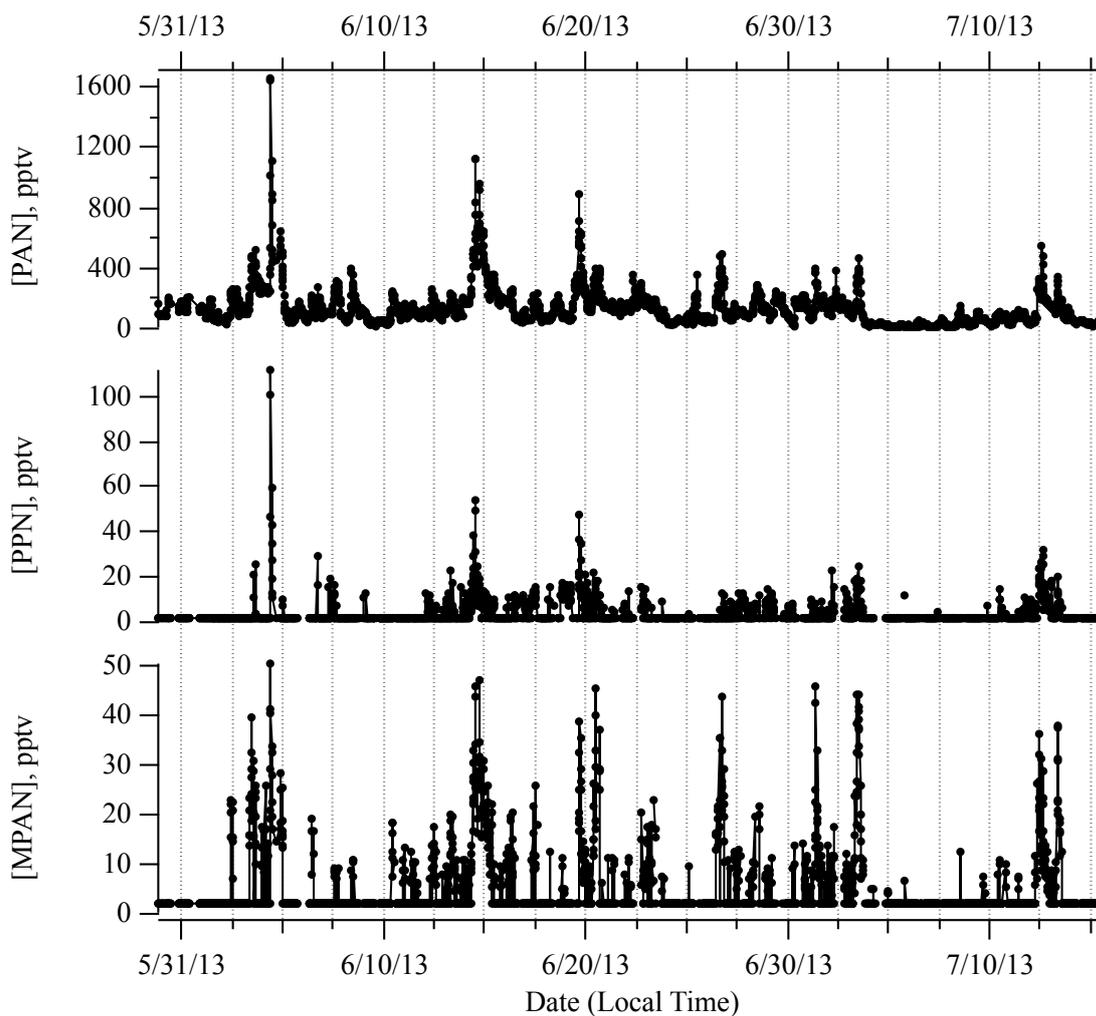
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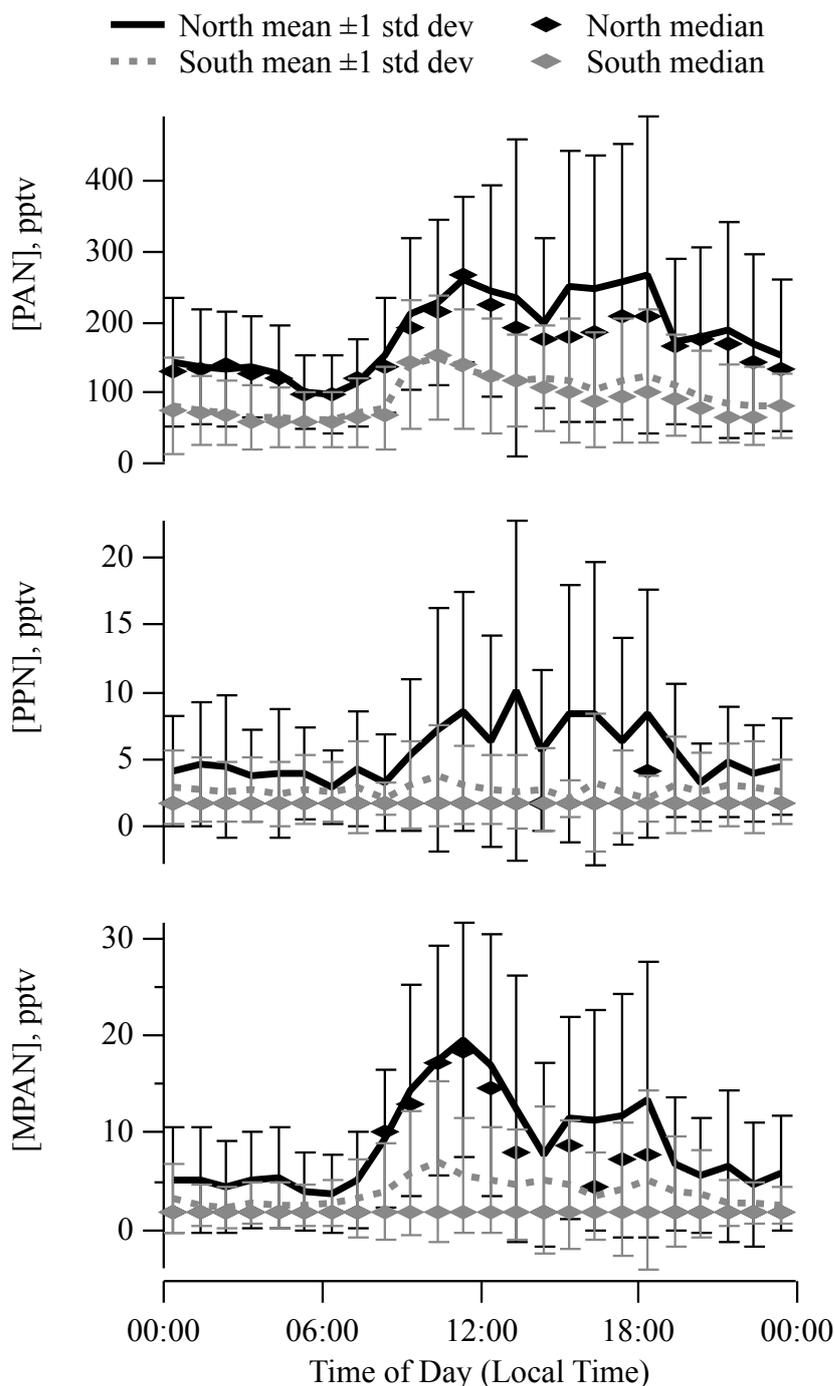
- 1 Table 1. General descriptive statistics of PANs and other trace gases during SOAS 2013 campaign.
 2 (Data on June 4th is not included.)

		All day	Daytime (10am–4pm)
PAN	Number of data	2813	719
	Mean ± STD (ppt)	126 ± 110	169 ± 129
	Median	99	148
PPN	Number of data	2402	534
	Mean ± STD (ppt)	4 ± 5	5 ± 7
	Median	2	2
MPAN	Number of data	2346	512
	Mean ± STD (ppt)	5 ± 7	9 ± 10
	Median	2	2
O ₃	Mean ± STD (ppb)	26 ± 13	34 ± 11
	Median	25	33
NO _x	Mean ± STD (ppb)	0.6 ± 0.6	0.3 ± 0.2
	Median	0.4	0.3
PANs/NO _y	Mean ± STD	0.11 ± 0.07	0.15 ± 0.08
	Median	0.10	0.14

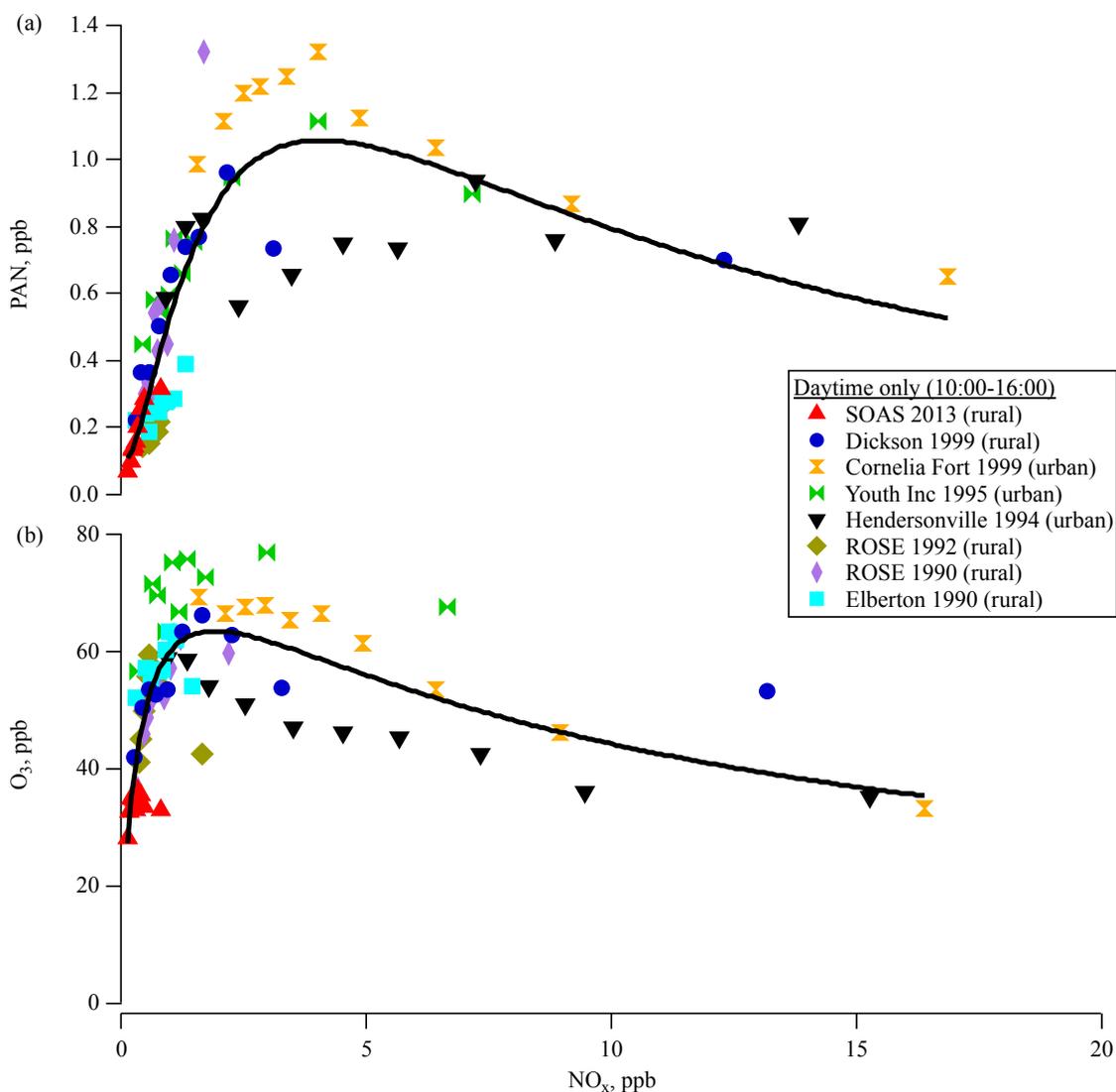
- 3 STD means standard deviation.
 4 PPN and MPAN include data of below detection limit, 1.8 and 1.9 pptv respectively.
 5 PANs = PAN + PPN + MPAN



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2 Figure 1. Time series of detected PAN, PPN, and MPAN during SOAS 2013 campaign using GC-ECD.



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2 Figure 2. Diurnal behaviors of PAN, PPN, and MPAN during SOAS 2013 with wind from South and
3 North. Data that were below detection limit (BDL) are included at half of the detection limit. The
4 medians of PPN and MPAN from the south were consistently BDL.

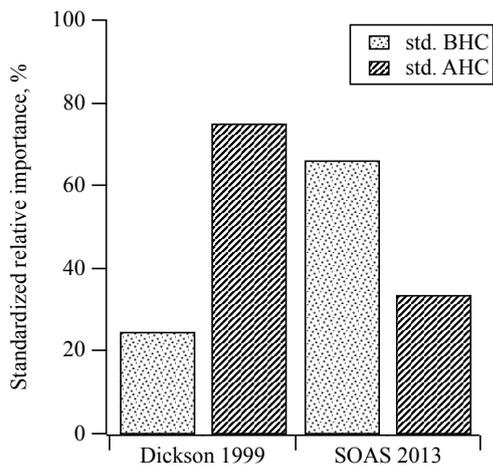


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Figure 3. Surface (a) PAN and (b) ozone concentrations for each ground site in the Southeastern U.S. over the last 23 years for 10 am – 4 pm as a function of the Concentration of NO_x in deciles. The solid line indicates a fit line for all measurements.



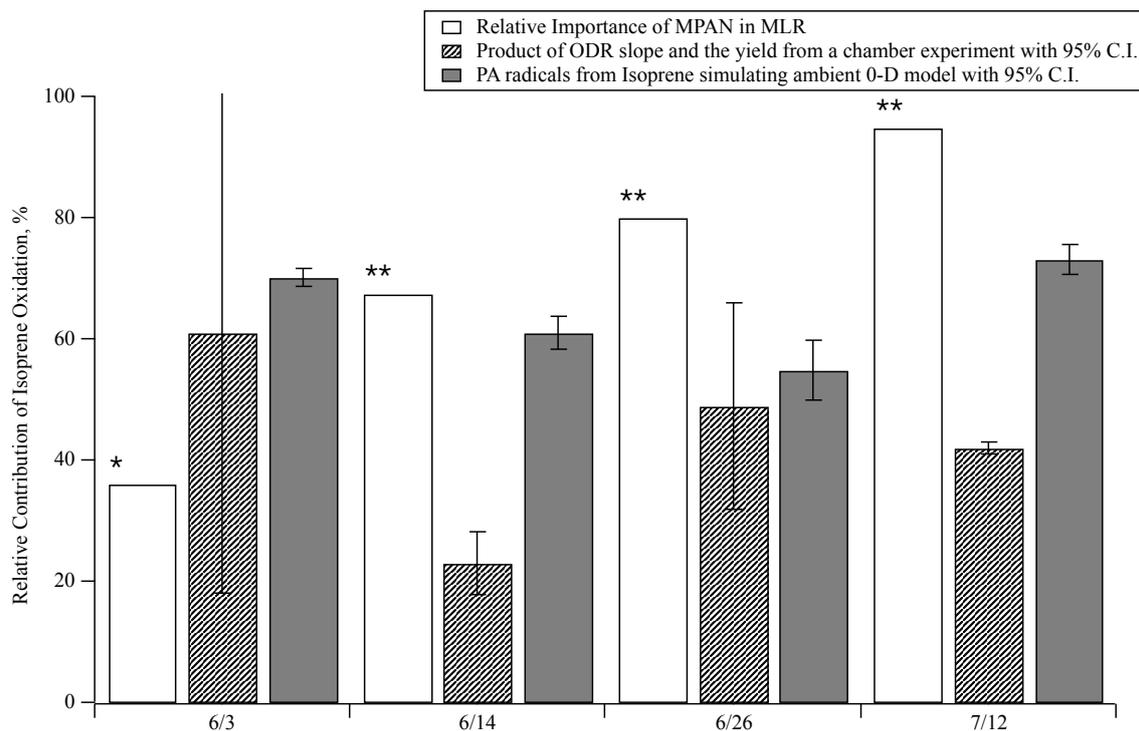
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3 Figure 4. Comparison of standardized relative contribution to PAN formation from biogenic and
4 anthropogenic hydrocarbons during the daytime in Dickson, TN in 1999 and SOAS, in Centreville, AL
5 in 2013. The std. BHC and std. AHC mean that standardized relative importance of biogenic
6 hydrocarbon and anthropogenic hydrocarbon respectively.

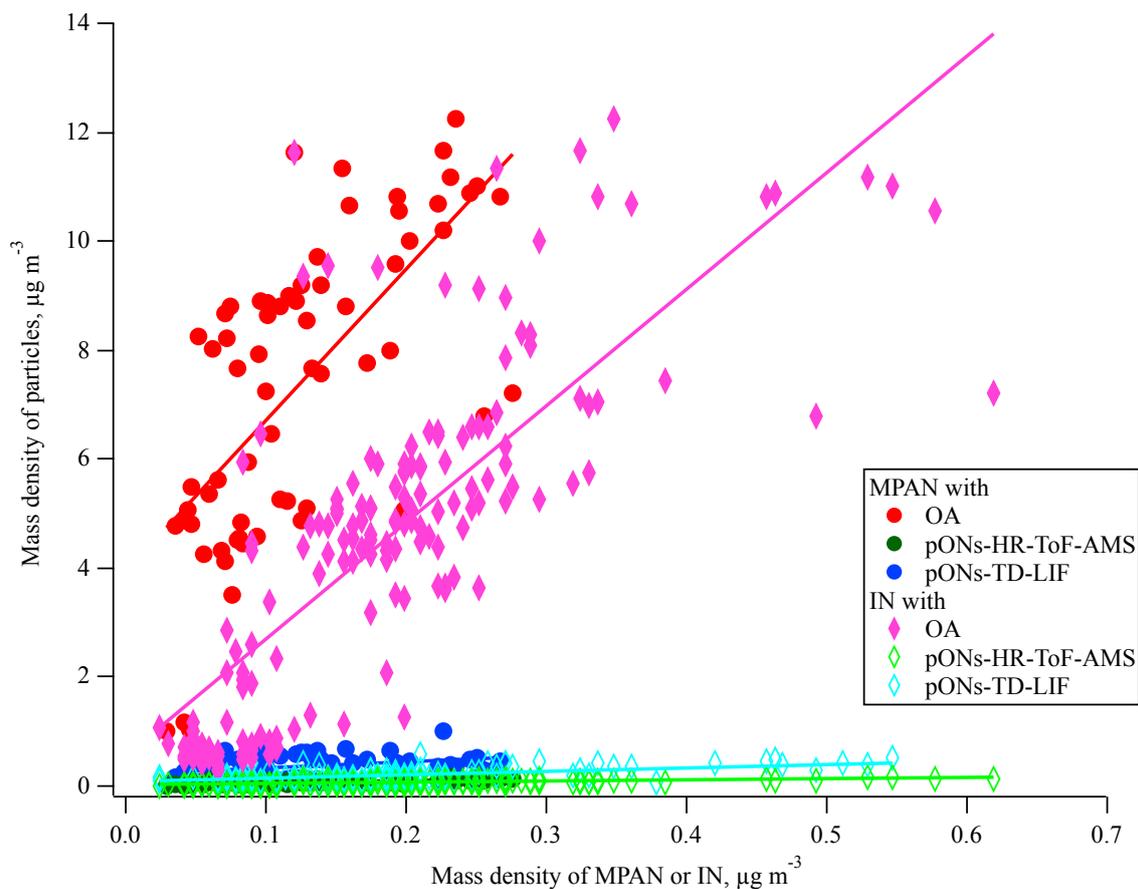
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* $P < 0.05$, ** $P < 0.001$

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Figure 5. Estimates of the relative contribution of isoprene oxidation to PANs formation during 4 specific days of SOAS 2013 using three different approaches: multiple regression analysis, ODR with chamber data, and simulation of PA radicals using a 0-D model. The P indicates the significant level of t-test. The C.I. means confidence interval.



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2 Figure 6. The relationship of mass between MPAN or IN in the gas phase and in organic aerosol for 10
3 am – 4 pm during June 29th – July 15th in SOAS 2013 (the time period when data on pONs-TD-LIF was
4 available). OA is organic aerosol (without organic nitrate) and pONs is particle-phase organic nitrates.
5 MPAN has a linear slope (R^2) of 27.8 (0.455) vs. OA, 0.4 (0.437) vs. pONs-HR-ToF-AMS, and 1.1 (0.120)
6 vs. pONs-TD-LIF. IN has a linear slope (R^2) of 21.4 (0.606) vs. OA, 0.2 (0.603) vs. pONs-HR-ToF-AMS,
7 and 0.6 (0.341) vs. pONs-TD-LIF.